

COAL LIQUEFACTION AND HYDROGEN
UTILIZATION AT LOW TEMPERATURES

B.C. Bockrath, E.G. Illig,
D.H. Finseth, and R.F. Sprecher

U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

The initial conversion of coal to material that may be extracted by polar solvents such as tetrahydrofuran or pyridine requires only relatively mild liquefaction conditions. The chemistry of the initial dissolution steps is very likely to be of great importance to the overall liquefaction process in that the yield and character of the initially formed products may greatly influence the success of subsequent liquefaction steps. Although conversion to the initial products seems to require a minimum of bond breaking, hydrogen-deuterium exchange reactions indicate that a rich chemistry transpires at the same time (1-4).

In the following experiments, the conversion of coal was examined as a function of several variables over the range of temperatures from 300°C to 450°C. The net change in both the content and the distribution of hydrogen among the products was followed using an analytical scheme based on elemental and NMR analyses. This method has been used to determine the net hydrogen utilization divided among categories for hydrogenation, hydrocarbon gas formation, heteroatom removal, and matrix bond breaking (5).

Experimental

Coal liquefaction was conducted in a 0.5-L stirred autoclave. In a typical experiment, 30 g (maf) of coal ground to pass 60 mesh was charged to the autoclave along with 70 g of coal-derived solvent. The solvent was a distillate cut (240°C-450°C) obtained from operations at the SRC-II pilot plant at Ft. Lewis, Wash. The autoclave was pressurized with the appropriate amount of hydrogen or nitrogen to obtain the desired operating pressure at temperature. Heat-up time to liquefaction temperatures was about 45 minutes. The autoclave was held at temperature for the specified time and then rapidly cooled by means of internal water-cooling coils. Grab samples of the off-gas were taken for analysis by gas chromatography as the autoclave was depressurized.

Conversion data in Figures 1 and 2 were obtained by first filtering the autoclave contents through a Whatman #541 filter on a Buchner funnel maintained at 60°C. The residue was then washed with tetrahydrofuran (THF) until the washings were nearly colorless. Data in Figure 3 were obtained by first digesting the liquid product from the autoclave with THF. The digest was vacuum-filtered through Whatman #2 filter paper, and the residue was washed with THF until the extract was nearly colorless. All residues were dried at 110°C and weighed. Conversion values were based on the weight of dried residue.

The methods used to determine hydrogen utilization data have been described (5). Data from the elemental analysis of the feed coal and liquefaction solvent, including the direct oxygen analysis, were used in these calculations (see Table 1). The liquid products were separated by Soxhlet extraction with methylene chloride. The carbon aromaticities were determined by ¹³C NMR using CP/MAS techniques on the insoluble fraction and high resolution ¹³C NMR in CD₂Cl₂ for the extract.

Results and Discussion

Liquefaction. The reactivities of the two bituminous coals are compared in Figure 1 as a function of temperature. The pronounced difference in reactivity at 325°C decreases rapidly with increasing liquefaction temperature. Although a difference in reactivity of these coals was expected, it is nonetheless remarkable that the conversion of the Illinois coal remains high even at a temperature as low as 325°C. The differences in patterns of hydrogen utilization discussed below are not striking for these two coals. The structural differences between the coals that are responsible for their individual responses to reaction temperature is a matter still open to question. At least, these data indicate that the choice of feedstock coal is even more critical for liquefaction at lower temperatures than at conventionally used temperatures.

The conversion of the Illinois coal is shown in Figure 2 as a function of reaction time after reaching temperature for three temperatures. It is evident that most conversion is complete within a short initial period of reaction even for the lowest of liquefaction temperatures. Undoubtedly, some of this conversion occurs during heat-up. Although conversion to low molecular weight products may require more severe conditions, the breakdown of the matrix structure of coal requires little time at modest temperatures. This same pattern of reactivity was noted earlier for liquefaction of coal in tetralin at 400°C (6). The present experiments show that the "prompt" yield of extract increases somewhat with temperature.

The effect of hydrogen pressure on conversion is quite significant. Figure 3 contains conversion data obtained at various temperatures and pressures of hydrogen or nitrogen. As expected, conversions increase with hydrogen pressure but hardly change with increasing nitrogen pressure. The sensitivity of conversion to hydrogen pressure is a function of liquefaction temperature. For example, increasing hydrogen pressure from zero to 2000 psi produces a larger increase in conversion at 400°C than at 350°C. It is not known whether this difference is related to the thermochemistry of bond scission reactions or to the state of reduction of pyrite in the mineral matter to pyrrhotite, which may act as a modest catalyst for coal liquefaction. Under these reaction conditions, analysis of the off-gases for H₂S and of the recovered mineral residues for pyrrhotite content shows that the reduction of pyrite is incomplete at 350°C. It is somewhat greater at 400°C, but probably not yet complete.

The character of the liquefaction solvent is well-known to have a major influence on conversion under conventional conditions. A number of experiments were made to determine whether conversions obtained at the relatively low temperatures employed here would be sensitive to modifications in the coal-derived liquefaction solvent. In one case, 10% of the weight of the coal-derived solvent was replaced by tetralin, a well-known hydrogen donor. Many studies have shown that coal conversion increases with minor addition of tetralin to a liquefaction solvent that is poor in donable hydrogen (7). Conversions were not changed within experimental error for reaction temperatures of 325°C, 350°C, and 400°C under hydrogen pressures of either 1000 or 2000 psig. Thus the amount of conversion under these conditions is not limited by lack of hydrogen donor compounds in the coal-derived solvent.

In a similar way, 10% of the weight of the coal-derived solvent was replaced by pyrene, a compound reported to be especially effective as both a hydrogen transfer agent (8) and a physical solvent for promoting liquefaction (9). Addition of this compound also had no effect within experimental error on conversion obtained at 350°C or 400°C under 1000 psig hydrogen. Taken together, these experiments indicate that for liquefaction at relatively low temperatures, the coal-derived solvent employed is not lacking in components suited for hydrogen donation, hydrogen shuttling, or physical solvation.

Hydrogen Utilization. A second set of autoclave experiments was performed to determine if changes in hydrogen distribution during liquefaction were different for coals of different reactivity. For initial experiments, the reaction conditions selected were 2000 psi hydrogen and 15 min. at various temperatures. In order to improve the reliability of the hydrogen distribution data, the work-up procedure was modified to use only solvents compatible with the NMR measurements needed to monitor hydrogenation. The entire contents of the autoclave were Soxhlet-extracted with methylene chloride to yield soluble and insoluble fractions. The yield of soluble material is less using methylene chloride, but residual solvent does not interfere with subsequent NMR aromaticity measurements. Both the soluble and insoluble fractions undergo elemental and NMR analysis. Thus, the relative amount of each fraction does not affect the values determined for the net amount of hydrogen used. For both coals, the gas yield was negligible at 300°C and 350°C, but increased to 1.2%-1.5% at 400°C and 8.2%-8.4% at 450°C on an maf basis.

The total hydrogen utilization is divided into four categories in Table 2. These results are arrived at using an analytical approach described previously (5). Entries in Table 2 give the net number of hydrogens incorporated (positive sign) or produced (negative sign) per 100 carbons of feed slurry. It must be emphasized that these numbers indicate only net changes in hydrogen involved in a particular mode of utilization and they include all the carbon in the whole feed slurry not just that in the coal. Negative numbers appearing in Table 2 for hydrogenation and matrix bond cleavage indicate that hydrogen (not necessarily in the form of H_2 gas) is being generated within the slurry by dehydrogenation (aromatization) or condensation reactions, respectively.

The data in Table 2 indicate that cracking reactions producing C_1 - C_4 hydrocarbon gases are not significant hydrogen consumers up to at least 400°C. Heteroatom removal increases with reaction temperature and is primarily oxygen removal under these conditions. (The maximum consumption by removal of N + S in these runs was 0.5 H/100 C for Illinois #6 at 450°C.) The higher content of labile oxygen of the Illinois #6 coal is reflected in Table 1.

The effect of temperature on the aromaticity of the total product (sols + insols + gases) is indicated in Figure 4. The trend to increasing product aromaticity with increasing temperature is the same for both coals. The data indicate that at low temperatures the net chemistry is hydrogenation, but above about 400° the total product aromaticity exceeds that of the feed slurry. This indicates that the net reaction above 400°C, even under 2000 psi hydrogen gas, is aromatization of the feed slurry (coal + solvent).

A similar pattern was observed in an earlier study of hydrogen utilization in a small continuous reactor, although in that case the magnitude of the variation of net hydrogenation with temperature was larger (5). This dominance of aromatization over hydrogenation at high temperatures is expected on thermodynamic grounds.

During liquefaction, bonds are being both broken (thermolysis) and formed (condensation). The category "matrix cleavage" in Table 2 attempts to quantitate the amount of hydrogen involved in bond-making/bond-breaking chemistry of the feed slurry. This value for the hydrogen involved in bond cleavage is necessarily determined by difference and thus should be interpreted with caution. With this warning it can be noted that for the Blacksville liquefaction experiments at 400°C and 450°C, the net hydrogen utilized in matrix cleavage is nil, indicating that any bond cleavage that occurs consuming hydrogen is balanced by condensation reactions producing hydrogen. At 325°C for the Blacksville coal, the data indicate net production of 2 hydrogens per 100 slurry carbons or a slight dominance of condensation reactions over thermolysis reactions. It is not unreasonable to expect condensation to predominate at low temperatures. The 325°C

experiments with Illinois #6 coal also indicate a predominance of condensation reactions, but the scatter of the data for the Illinois #6 coal liquefaction experiments is too high to comment on with confidence.

The net amount of hydrogen consumed in matrix cleavage is a measurement of the resultant of two opposing reaction routes and is thus expected to be a function of solvent type, reaction time, catalyst, coal, and temperature. The response of hydrogen utilization to these variables is now under investigation. The present data form a baseline for future comparisons. Improvements in the analytical method will make it easier to form firm conclusions on the relative importance of condensation versus thermolysis as a function of reaction conditions.

It is interesting to note, however, that both in this work (325°C data) and in the previous study of continuous unit operation, there is evidence for the dominance of condensation reactions under mild conditions. The analytical approach used to generate the data in Table 2 is still undergoing refinement, but it appears that it may be quite useful for characterizing differences in liquefaction chemistry and their dependence on reaction conditions.

REFERENCES

1. J.A. Franz, Fuel, 58, 405 (1979).
2. I.B. Goldberg, H.R. Crowe, J.J. Ratto, R.P. Skowronski, and L.A. Heredy, Fuel, 59, 133 (1980).
3. M.A. Wilson, P.J. Collin, P.F. Barron, and A.M. Vassallo, Fuel Processing Technology, 5, 281 (1982).
4. F.K. Schweighardt, B.C. Bockrath, R.A. Friedel, and H.L. Retcofsky, Anal. Chem., 48, 1254 (1976).
5. D.H. Finseth, B.C. Bockrath, D.L. Cillo, E.G. Illig, R.F. Sprecher, H.L. Retcofsky, and R.G. Lett, Am. Chem. Soc. Div. Fuel Chem. Preprints, 28(5), 17 (1983).
6. R.C. Neavel, Fuel, 55, 237 (1976).
7. B.C. Bockrath, in "Coal Science," (M.L. Gorbaty, J.W. Larsen, and I. Wender, Eds.) Vol. 2, pp. 65-124, Academic Press, NY (1983).
8. F.J. Derbyshire and D.D. Whitehurst, Fuel, 60, 655 (1981).
9. I. Mochida, A. Takerabe, and K. Takeshita, Fuel, 58, 17 (1979).

Reference in the report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

TABLE 1. ELEMENTAL ANALYSES, MAF

	C	H	N	O	S
BLACKSVILLE COAL	80.6	5.6	1.4	9.4	3.1
ILLINOIS #6 COAL	73.7	5.6	1.5	14.8	4.5
SOLVENT	87.1	8.0	1.4	5.0	0.4

MOISTURE FREE ASH CONTENTS WERE BLACKSVILLE = 11.9%, ILLINOIS #6 = 13.6%,
SOLVENT < 0.1%.

TABLE 2.
HYDROGEN UTILIZATION VS. COAL REACTIVITY
AND TEMPERATURE: HYDROGENS INCORPORATED
PER 100 CARBONS OF FEED SLURRY

FATE OF HYDROGEN	BLACKSVILLE #2			ILLINOIS #6					
	325°	400°	450°	300°	300° Dup.	325°	400°	450°	450° Dup.
Gas Make	0	0	3	0	0	0	0	3	3
Heteroatom Removal	0	1	1	1	0	1	2	3	3
Hydrogenation	1	-2	-3	1	1	2	0	-3	-3
Matrix Cleavage	-2	0	0	0	+2	-2	+2	-1	0
TOTAL	-1	-1	+1	+2	+3	+1	+4	+2	+3

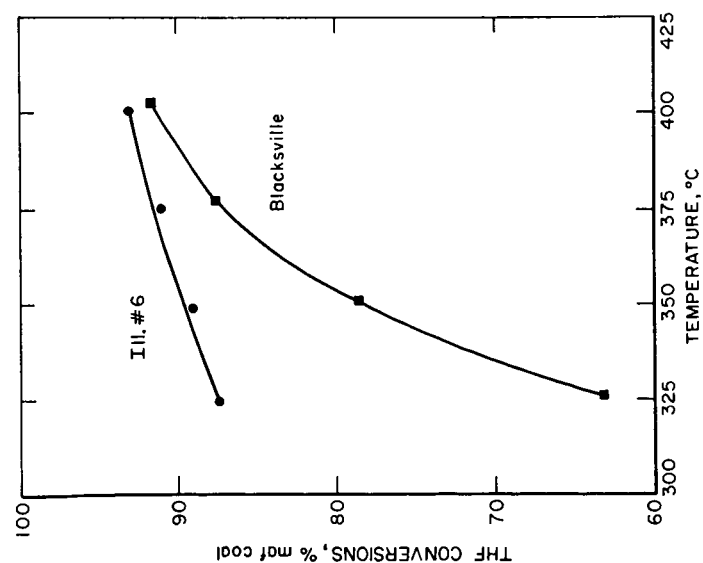


Figure 1- Conversion of two coals versus temperature at 2000 psi hydrogen for 60 minutes.

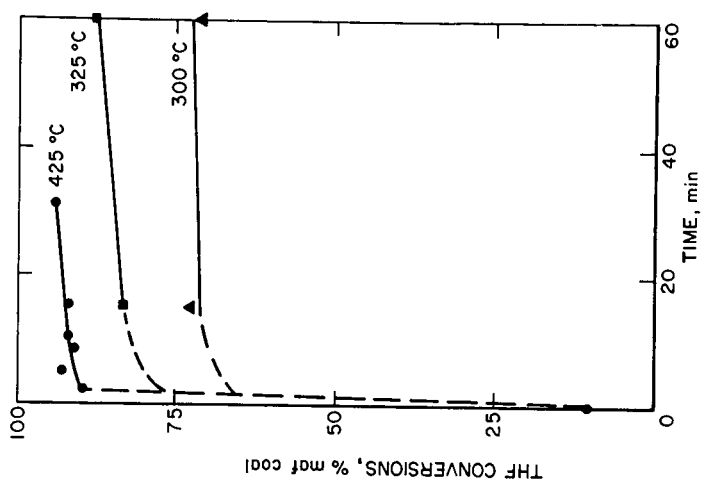


Figure 2- Conversion of Illinois #6 (River King) Coal at 2000 psi hydrogen.

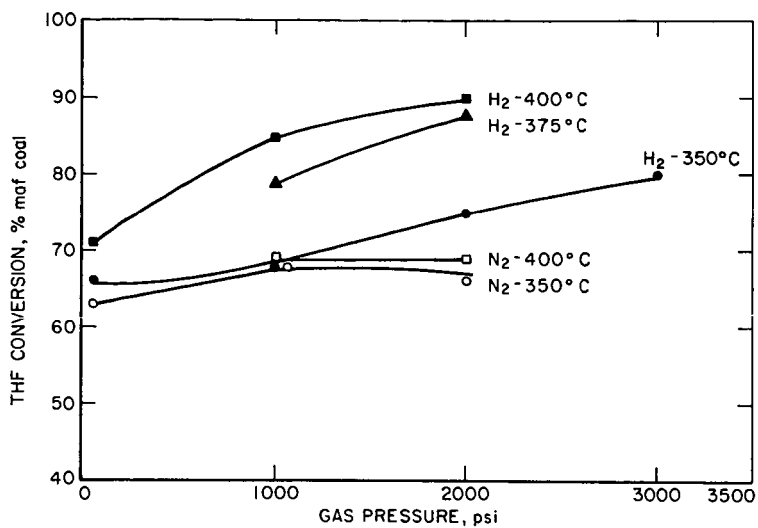


Figure 3 - Pressure effect at various temperatures on Illinois # 6 coal, 15 min at temperature.

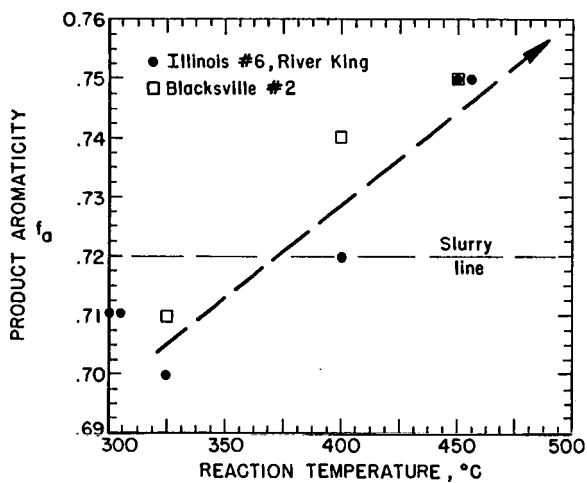


Figure 4. Product Aromaticity Versus Reaction Temperature for Blacksville #2 and Illinois #6